

MEASUREMENTS OF THE LIGHT-ABSORBING MATERIAL INSIDE CLOUD DROPLETS  
AND ITS EFFECT ON CLOUD ALBEDO

C. H. Twohy<sup>1,3</sup>, A. D. Clarke<sup>2</sup>, S. G. Warren<sup>1</sup>, L. F. Radke<sup>1</sup>, and R. J. Charlson<sup>1</sup>

The question of how aerosol pollutants affect the radiative properties of clouds was posed by Twomey [1977], who pointed out that aerosols have two competing effects: they increase the number of particles which might act as cloud condensation nuclei (CCN), but also include materials such as elemental carbon (EC) which are essentially black to solar radiation. Elevated levels of CCN, assumed to result in greater numbers of smaller droplets, would lead to brighter, more reflective clouds, while enhanced absorption due to carbon particles could potentially make clouds darker. Based on the global distribution of cloud cover and absorption measurements which Twomey et al. [1984] used in a later paper, the overall climatic effect of increasing pollution over time was shown by their model to be cooling, of the same order of magnitude as predicted warming from the greenhouse effect of CO<sub>2</sub> alone.

Cloud absorptance values measured directly by aircraft [Reynolds et al., 1975; Stephens et al., 1978] are frequently much higher than those which are theoretically calculated from measured microphysical parameters. One possible explanation of this phenomenon is absorption of radiation by aerosol particles within the cloud. In a comparison of measured and computed reflectance spectra at various wavelengths, Twomey and Cocks [1982] concluded that this process could not be the major explanation since the observed enhanced absorption predominated not at visible wavelengths, but in the near infrared where absorption by particles should be negligible relative to that by liquid water and ice.

Most of the measurements of light-absorbing aerosol particles made previously have been in non-cloudy air and therefore provide no insight into aerosol effects on cloud properties. In this paper, we describe an experiment designed to measure light absorption exclusively due to substances *inside* cloud droplets, compare the results to related light absorption measurements, and evaluate possible effects on the albedo of clouds. The results of this study validate those of Twomey and Cocks and show that the measured levels of light-absorbing material are negligible for the radiative properties of realistic clouds.

Elemental carbon (EC) is the most efficient light-absorbing material present in the atmosphere, and except in unusual cases absorption by aerosols is dominated by elemental carbon [Rosen et al., 1978; Heintzenberg, 1982; Clarke and Charlson, 1985]. It is possible for hydrophobic carbon particles to obtain a hygroscopic coating and be incorporated into clouds by nucleation scavenging. Measurement of EC in cloud droplets, however, is problematic due to the difficulty in collecting cloud droplets separately from interstitial aerosol particles and the tendency of EC to stick to surfaces of collection vessels [Ogren, 1983]. In addition, identification of EC requires relatively long sampling times in many environments. In order to eliminate the first difficulties, cloud droplets were sampled in this experiment with a counterflow virtual impactor (CVI), a probe which by inertial impaction collects only droplets above a certain minimum radius while effectively rejecting interstitial aerosol particles [Ogren et al., 1985; Noone et al., 1988]. The CVI evaporates droplets (leaving the non-volatile aerosol residue) before they touch any surface, minimizing sample contamination and loss of carbon particles to the walls of the sampler. The long sampling time requirement was avoided through the use of a very sensitive technique for measuring the absorption of light by the droplet residue particles. The "Integrating Sandwich Method" [Clarke, 1982], enhances light absorption by particles in the sample by confining them between two highly reflecting surfaces.

<sup>1</sup>Department of Atmospheric Sciences, University of Washington, Seattle, Washington 98195.

<sup>2</sup>Hawaii Institute of Geophysics, University of Hawaii, Honolulu, Hawaii 96822.

<sup>3</sup>Currently at National Center for Atmospheric Research, Boulder, Colorado 80307-3000.

Cloud droplets were sampled by the CVI on the University of Washington's C-131 aircraft in the FIRE project off the Southern California coast in June and July, 1987. Droplets above five  $\mu\text{m}$  (calculated cut radius) were collected on five different days for light absorption analysis of the droplet residue particles, which were impacted onto Nuclepore polycarbonate filters. The C-131 typically flew at cloud base, above the cloud, or inside the cloud for periods of twenty to thirty minutes at an airspeed of 80-85 meters  $\text{s}^{-1}$  with occasional shallow descents or ascents through the stratus deck. Sampling times in cloud ranged from 22 to 143 minutes, resulting in collection of droplets from about 3-20 cubic meters of cloudy air.

Absorption coefficients representing the absorption per unit length of droplet-laden air were calculated directly from the amount of light absorption by the filter sample and the sample volume of air. Model trajectories [Kloesel et al., 1988] revealed that air reaching the 925 mb level had been located west, northwest, or north of the project area on the days prior to the flights, and windspeeds were highly variable. Examination of the droplet size spectrum measured by the Forward Scattering Spectrometer Probe (FSSP) on the aircraft indicated that some occasions, the air appeared to be of marine origin but many times the spectra showed continental influence. Four of the measured absorption coefficients for the droplet residue ranged from 6 to  $20 \times 10^{-8} \text{ m}^{-1}$ , while one (from July 7, 1987) exhibited much less absorption. The absorption coefficients were generally higher than those measured in aerosol at remote locations such as Mauna Loa Observatory [Clarke and Charlson, 1985] and the South Pole [Clarke et al., in preparation], and fell within the range measured at Hurricane Ridge on the western coast of Washington State [Clarke, 1982]. They were, however, much lower than those typical of extremely polluted air at industrially influenced locations like St. Louis, Missouri [Weiss, 1980].

The mass concentration of elemental carbon inside the droplets was estimated from the measured absorption coefficients and the liquid water content, with the assumption that all absorption was due to elemental carbon with a mass absorption coefficient of  $10 \text{ m}^2 \text{ g}^{-1}$ . Resulting concentrations of EC in cloud water were 23-79  $\text{ng EC g}^{-1}$  for four of the five cases. These values were comparable with those measured in rainwater [Ogren, 1983] at Seattle, Washington and at less polluted sites in Sweden. Samples of interstitial particles were also taken during the project, but were analyzed for light absorption by a less sensitive method, and all were below the detection limit. From these results an absolute upper bound on the concentration of interstitial elemental carbon (IEC) was established for each flight.

The maximum possible effect of the measured EC on cloud albedo was determined by calculating albedo at wavelength 0.475  $\mu\text{m}$  where liquid water has its weakest absorption [Hale and Querry, 1973], by using the largest measured in-cloud EC concentrations, and by assessing the effect upon an optically "semi-infinite" cloud. In another scenario but still at the most sensitive wavelength, the effect of EC on the albedo of a more realistic (thinner) cloud was evaluated. The surface-area-weighted or "effective" mean radius [Hansen and Travis, 1974],  $r_{\text{eff}}$ , which determines the effect of the droplet size distribution on the single-scattering albedo,  $\omega$ , was calculated and averaged for each sampling period from the FSSP data, and the Mie program of Wiscombe [1980] was used to obtain values for  $\omega$ , asymmetry factor, and extinction efficiency.

Figures 1 and 2 show the calculated effect of elemental carbon on the albedo of clouds with different  $r_{\text{eff}}$  values. Figure 1 applies to a semi-infinite cloud (optical thickness  $\tau^* = \infty$ ) with the shaded area representing the range of EC concentrations under consideration, explained in more detail in the figure caption. Curved lines show the effect of different  $r_{\text{eff}}$  values on albedo, with a greater albedo reduction resulting when EC is present in larger droplets. If an  $r_{\text{eff}}$  of 10  $\mu\text{m}$  (slightly larger than the ones calculated) is assumed, the change in the albedo of this semi-infinite cloud due to the carbon concentrations considered ranges from -0.014 to -0.029. EC has less effect on albedo as optical thickness decreases, and Figure 2 shows the results for a more realistic cloud with  $\tau^* = 30$ . (The calculated optical thicknesses of the FIRE clouds during the five sampling periods were all smaller than 30, so their albedos should be slightly less affected.) Assuming the same  $r_{\text{eff}}$  and range of EC concentrations as before, the reduction in albedo in this case is only 0.001 even under the most stringent circumstances. Due to the higher absorption of water at

wavelengths other than 0.475  $\mu\text{m}$ , reduction in spectrally-averaged albedos will be approximately half as large as those presented here.

We have found, therefore, that for the measured clouds which appear to have been moderately polluted, the amount of EC present was insufficient to affect albedo. Much higher contaminant levels or much larger droplets than those measured would be necessary to significantly alter the radiative properties. The effect of the concentrations of EC actually measured on the albedo of snow, however, would be much more pronounced since in contrast to clouds, snowpacks are usually optically semi-infinite and have large particle sizes.

**Acknowledgements:** This work was supported in part by NSF grant ATM-86-07377 and the Defense Nuclear Agency, through funds made available under document 57-0343 from Sandia National Laboratory. Radiative transfer calculations were made at NCAR and supported by NSF grant ATM-86-05134. We thank David Covert, Kevin Noone, and Steven Domonkos for their invaluable advice and aid in installing instruments aboard the aircraft. Thanks also are due to John Ogren and Jost Heintzenberg for building the first CVI.

**Note:** The full version of this paper is in preparation for the *Journal of Geophysical Research*.

- Bohren, C. F., and D. R. Hoffman, in *Absorption and scattering of light by small particles*, p.446, Wiley-Interscience, New York, 1983.
- Chylek, P., Ramaswamy, V., and V. J. Srivastava, Albedo of soot-contaminated snow, *J. Geophys. Res.*, 88, 10837-10843, 1983.
- Clarke, A. D., Integrating Sandwich: a new method of measurement of the light absorption coefficient for atmospheric aerosols, *Appl. Opt.*, 21, 3011-3020, 1982.
- Clarke, A. D., and R. J. Charlson, Radiative properties of the background aerosol: absorption component of extinction, *Science*, 229, 263-265, 1985.
- Clarke, A. D., Warren, S. G., and T. C. Grenfell, Soot in the atmosphere and snow surface of Antarctica, *J. Geophys. Res.*, in preparation.
- Hale, G. M., and M. R. Querry, Optical constants of water in the 200-nm to 200- $\mu\text{m}$  wavelength range, *Appl. Opt.*, 12, 555-562, 1973.
- Hansen, J. E., and L. D. Travis, Light Scattering in Planetary Atmospheres, *Space Sci. Rev.*, 16, 527-610, 1974.
- Heintzenberg, J., Size-segregated particulate elemental carbon and aerosol light absorption at remote Arctic locations, *Atmos. Env.*, 16, 2461-2469, 1982.
- Kloesel, K. A., Albrecht, B. A., and D. P. Wyle, FIRE marine stratocumulus observations--summary of operations and synoptic conditions, Penn State University, 1988.
- Noone, K. J., Charlson, R. J., Covert, D. S., Ogren, J. A. and J. E. Heintzenberg, Design and calibration of a counterflow virtual impactor for sampling of atmospheric fog and cloud droplets. Accepted in *Aer.Sci.and Tech.*, 1988.
- Ogren, J. A., Elemental carbon in the atmosphere, Ph.D. dissertation, University of Washington, Seattle, 1983.
- Ogren, J. A., Heintzenberg, J., and R. J. Charlson, In-situ sampling of cloud droplets with a droplet to aerosol converter, *Geophys. Res. Lett.*, 12, 121-124, 1985.
- Rosen, H., Hansen, D. A., Gundel, L., and T. Novakov, Identification of the optically absorbing component in urban aerosols, *Appl. Opt.*, 17, 3859-3861, 1978.
- Stephens, G., Paltridge, G., and C. Platt, Radiation profiles in extended water clouds. III: Observations, *J.Atmos. Sci.*, 35, 2133-2141, 1978.
- Twomey, S., The influence of pollution on the short-wave albedo of clouds, *J. Atmos Sci.*, 34, 1149-1152, 1977.
- Twomey, S., and T. Cocks, Spectral reflectance of clouds in the near-infrared: comparison of measurements and calculations, *J. Meteor. Soc. Jap.*, 60, 583-592, 1982.
- Twomey, S. A., Piepgrass, M., and T. L. Wolfe, An assessment of the impact of pollution on global cloud albedo, *Tellus*, 36B, 356-366, 1984.
- Weiss, R. E., The optical absorption properties of suspended particles in the lower troposphere at visible wavelengths, Ph.D. dissertation, University of Washington, Seattle, 1980.
- Wiscombe, W. J., Improved Mie scattering algorithms, *Appl. Opt.*, 19, 1505-1509, 1980.

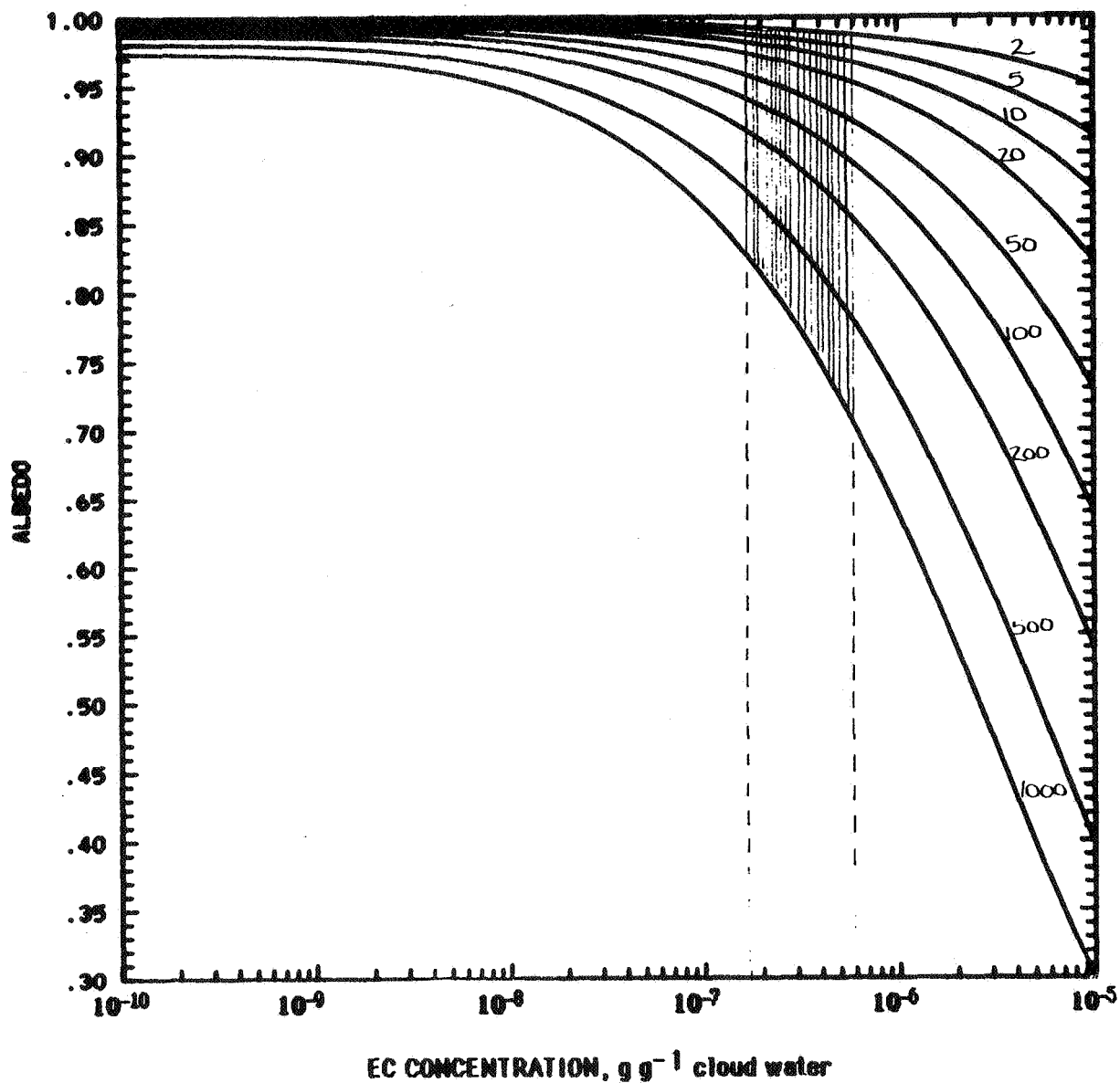


Figure 1. The effect of different concentrations of elemental carbon (EC) on the albedo of a semi-infinite cloud (optical thickness =  $\infty$ ) at  $\lambda = 0.475 \mu\text{m}$ , with curved lines representing different values of effective droplet radii in  $\mu\text{m}$ . The shaded area represents the range of concentrations under consideration: from  $1.6 \times 10^{-7}$  which assumes the only EC in the cloud is the maximum amount measured *inside* droplets, to  $5.9 \times 10^{-7}$  which includes the maximum possible value for interstitial carbon as well. Since calculations modeled EC as an external mixture, the inside-droplet value was doubled to account for the enhanced absorption of EC inside water droplets [Chylek, 1983; Bohren, 1983].

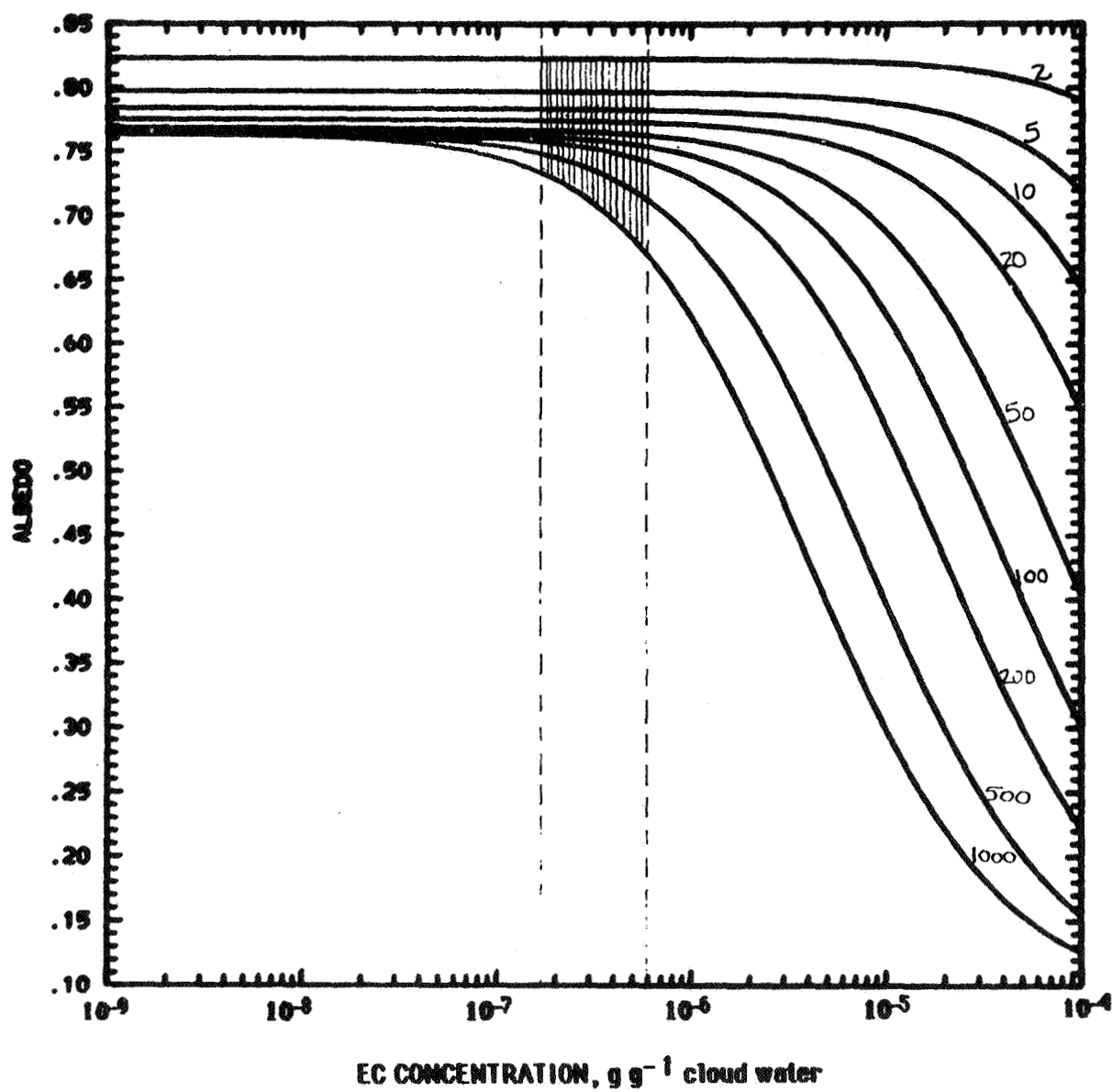


Figure 2. Same as Figure 1 except with a more realistic optical thickness of 30.